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Magnetic properties and crystal structure of $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$

D. Mikhailova,^{1,2} B. Schwarz,² A. Senyshyn,³ A. M. T. Bell,⁴ Y. Skourski,⁵ H. Ehrenberg,^{2,6} A. A. Tsirlin,¹ S. Agrestini,¹ M. Rotter,¹ P. Reichel,^{1,2} J. M. Chen,⁷ Z. Hu,¹ Z. M. Li,⁷ Z. F. Li,⁷ and L. H. Tjeng¹

¹Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Str. 40, D-01187 Dresden, Germany

²Institute for Complex Materials, IFW Dresden, Helmholtzstr. 20, D-01069 Dresden, Germany

³Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM-II), Technische Universität München, Lichtenbergstr. 1, D-85747 Garching near München, Germany

⁴Hamburger Synchrotronstrahlungslabor am Deutschen Elektronen-Synchrotron, Notkestr. 85, D-22607 Hamburg, Germany

⁵Dresden High Magnetic Field Laboratory, Forschungszentrum Dresden-Rossendorf, D-01314 Dresden, Germany

⁶Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

⁷National Synchrotron Radiation Research Center (NSRRC), 101 Hsin-Ann Road, Hsinchu 30077, Taiwan

(Received 1 April 2012; revised manuscript received 7 September 2012; published 10 October 2012)

We have studied the magnetic properties and crystal structure of $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$ as a function of temperature. Two characteristic temperatures, $T_1 = 90$ K and $T_2 = 25$ K for $\text{Sr}_3\text{CoIrO}_6$, and $T_1 = 85$ K and $T_2 = 15$ K for $\text{Sr}_3\text{NiIrO}_6$, were observed. Below T_1 a significant increase of magnetization and below T_2 a weak temperature dependence of magnetization in the field-cooled and practically zero magnetization values in the zero-field-cooled mode were detected for both compounds. The existence of Ir^{4+} in $\text{Sr}_3\text{CoIrO}_6$ was confirmed by an $\text{Ir}-L_{\text{III}}$ x-ray absorption measurement. Magnetoelastic effects have been observed in the temperature dependence of the lattice parameters of $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$. The magnetic structure of $\text{Sr}_3\text{CoIrO}_6$ in zero fields can be described as a commensurate modulated antiferromagnet with a propagation vector $\mathbf{k} = (0, 0, 1)$. Neutron powder diffraction with polarized neutrons gave evidence of short-range magnetic order, above and below the magnetic ordering temperature.

DOI: 10.1103/PhysRevB.86.134409

PACS number(s): 75.25.-j, 71.70.Ej, 61.05.fm

I. INTRODUCTION

Among numerous isostructural phases with $\text{A}_3\text{MM}'\text{O}_6$ stoichiometry (M and M' are transition metals), six of them, $\text{Ca}_3\text{Co}_2\text{O}_6$,^{1,2} $\text{Ca}_3\text{CoRhO}_6$,³⁻⁸ $\text{Ca}_3\text{CoIrO}_6$,^{9,10} $\text{Sr}_3\text{NiRhO}_6$,¹¹ $\text{Sr}_3\text{NiIrO}_6$,^{12,13} and the recently reported $\text{Sr}_3\text{Co}_2\text{O}_6$,¹⁴ seem to exhibit similar magnetic behavior. This is surprising considering the different magnetic cations and their different electronic states. For example, in $\text{Ca}_3\text{Co}_2\text{O}_6$, the presence of both high-spin Co^{3+} (HS-Co^{3+} , d^6 , $S = 2$) and nonmagnetic low-spin Co^{3+} (LS-Co^{3+} , d^6 , $S = 0$) states was established.^{15,16} A similar scenario can be envisaged for $\text{Sr}_3\text{Co}_2\text{O}_6$. On the other hand, a HS-Co^{2+} (d^7 , $S = 3/2$) state in combination with LS-Rh^{4+} (d^5 , $S = 1/2$) and LS-Ir^{4+} (d^5 , $S = 1/2$) configurations were determined for $\text{Ca}_3\text{CoRhO}_6$,^{7,17} and $\text{Ca}_3\text{CoIrO}_6$,¹⁰ respectively. Moreover, HS-Ni^{2+} (d^8 , $S = 1$) and $\text{LS-Ir}^{4+}/\text{LS-Rh}^{4+}$ states were deduced for $\text{Sr}_3\text{NiIrO}_6$,¹²/ $\text{Sr}_3\text{NiRhO}_6$.¹¹

The crystal structure of these compounds is built of chains of face-sharing MO_6 trigonal prisms ($M = \text{Co}, \text{Ni}$) and $\text{M}'\text{O}_6$ octahedra ($M' = \text{Co}, \text{Rh}, \text{Ir}, \text{Mn}$) stacked along the c axis. The chains are separated by Sr or Ca cations and form a triangular lattice. The magnetism of these compounds can be characterized by two temperatures: (1) below T_1 a complex antiferromagnetic order appears and magnetic phase transitions in applied field lead to a nonlinear evolution of the magnetization; (2) below $T_2 < T_1$ a spin-freezing state was proposed. Note that for $\text{Ca}_3\text{CoIrO}_6$ only a spin-freezing temperature T_2 was reported.¹⁰

For $\text{Ca}_3\text{Co}_2\text{O}_6$ and $\text{Ca}_3\text{CoRhO}_6$ a partially disordered antiferromagnetic (PDA) interchain and a ferromagnetic intrachain Co type of order were observed by neutron diffraction.^{2,4} Replacement of octahedrally coordinated LS-

Co^{3+} in $\text{Ca}_3\text{Co}_2\text{O}_6$ by LS-Rh^{4+} increases the magnetic ordering temperature T_1 from 25 to 90 K.

$\text{Sr}_3\text{CoIrO}_6$ has been recently synthesized for the first time¹⁸ and is isostructural to the materials discussed previously. Thus magnetic properties similar either to $\text{Ca}_3\text{CoRhO}_6$ or to $\text{Ca}_3\text{CoIrO}_6$ can be expected. By comparing $\text{Ca}_3\text{CoRhO}_6$, $\text{Ca}_3\text{CoIrO}_6$, $\text{Sr}_3\text{NiIrO}_6$, and $\text{Sr}_3\text{CoIrO}_6$ it is possible to disentangle the influence of different degrees of freedom such as electronic configuration (d^7 for Co^{2+} and d^8 for Ni^{2+}) or spin state and geometric criteria such as the interchain distances due to the different cation radii of $\text{Ca}^{2+}/\text{Sr}^{2+}$. The magnetic $4d$ - and $5d$ -cations Rh and Ir contribute a much smaller magnetic moment than Co and Ni. Up to now, only for $\text{Ca}_3\text{CoRhO}_6$ magnetic Bragg reflections were observed by neutron powder diffraction below T_1 .^{3,4} At temperatures down to T_2 , a PDA state was inferred. In the magnetic phase 2/3 of the ferromagnetic chains are coupled antiferromagnetically while the other 1/3 of the chains stays disordered, with a spin orientation along the c axis either in “positive” or “negative” direction.⁴ This exotic magnetic state might be the consequence of an antiferromagnetic interchain interaction on the triangular lattice and has been discussed for $\text{Ca}_3\text{CoRhO}_6$ and $\text{Sr}_3\text{NiIrO}_6$. An even more complex glassy-type magnetic behavior without PDA was proposed for $\text{Ca}_3\text{CoIrO}_6$.¹⁰ For a field-oriented crystalline sample of $\text{Ca}_3\text{CoRhO}_6$ a saturated magnetization of about $4 \mu_B/\text{formula units (f.u.)}$ was observed at 4 T between T_2 and T_1 , corresponding to a ferromagnetic alignment of HS-Co^{2+} and LS-Rh^{4+} on all three chains.³ A very large orbital magnetic moment of HS-Co^{2+} ions of about $1.7 \mu_B$ was predicted theoretically¹⁵ and found in $\text{Ca}_3\text{CoRhO}_6$ by x-ray absorption and x-ray magnetic dichroism experiments.¹⁷

In contrast, for $\text{Ca}_3\text{CoIrO}_6$ ¹⁰ and $\text{Sr}_3\text{NiIrO}_6$ ¹² the magnetization does not saturate even at much higher fields. Differences in the magnetic behavior of $\text{Ca}_3\text{Co}_2\text{O}_6$, $\text{Ca}_3\text{CoRhO}_6$, and $\text{Ca}_3\text{CoIrO}_6$ were attributed to the different strengths of magnetic interchain and intrachain interactions, which are reflected by the c/a ratio of the underlying crystal structure.¹⁰ The c/a ratio increases in the series $\text{Ca}_3\text{CoM}'\text{O}_6$ from 1.143 ($M' = \text{Co}$) via 1.166 ($M' = \text{Rh}$) to 1.189 ($M' = \text{Ir}$). However, this is a very simplified view in the light of the complex interchain magnetic exchange interactions, as discussed, for example, for $\text{Ca}_3\text{Co}_2\text{O}_6$ in Ref. 2.

In the present work we studied two compounds, $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$, which are very close from the crystallographic point of view but different in their electronic configuration. Magnetic properties have been measured in static and pulsed magnetic fields up to 60 T between 1.8 and 350 K. The temperature evolution of the lattice parameters was determined by synchrotron powder diffraction, and the time dependence of the magnetization process was studied at temperatures near the spin-freezing transition at T_2 . Powder diffraction measurements using unpolarized, and polarized neutron beams from room temperature down to 4 K were performed on $\text{Sr}_3\text{CoIrO}_6$.

II. EXPERIMENTAL

A. Synthesis and sample characterization

$\text{Sr}_3\text{M}'\text{IrO}_6$ samples were prepared by solid state reactions in an Ar atmosphere at 1473 K for 24 h from stoichiometric powder mixtures of CoO for $M' = \text{Co}$ and NiO for $M' = \text{Ni}$ (Alfa Aesar, 99.999%) with IrO_2 (Umicore) and SrCO_3 (Alfa Aesar, 99.99%).¹⁸ The phase analysis and the determination of unit cell parameters was based on x-ray powder diffraction (XPD) done on a STOE STADI P diffractometer (Co- $K\alpha_1$ -radiation) in flat-sample transmission mode. The $\text{Sr}_3\text{CoIrO}_6$ contained a tiny amount of metallic Ir (0.8 wt.%) that does not affect any of the results presented subsequently. The $\text{Sr}_3\text{NiIrO}_6$ sample was single phase.

B. X-ray absorption spectroscopy

The Ir- L_{III} x-ray absorption spectra (XAS) of $\text{Sr}_3\text{CoIrO}_6$ and of an Ir^{4+} reference compound $\text{Sr}_3\text{ZnIrO}_6$, prepared according to Ref. 19, were recorded at the 01C beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan, which is equipped with a double-crystal Si(111) monochromator. Both Ir- L_{III} spectra were collected under identical conditions applying the bulk sensitive fluorescence yield method using a Lytle detector. The photon energy resolution for the present set-up was 1.5 eV at the Ir- L_{III} edge ($\sim 11,218$ eV), for energy calibration the L_{III} edge of Pt (at 11,564 eV) was used.

C. Magnetic measurements

The temperature dependence of the magnetization was measured both in zero-field-cooled (ZFC) and in field-cooled (FC) mode between $T = 1.8$ and 350 K. The field dependence of the magnetization up to 9 T was determined using a magnetic property measurement system MPMS XL7 equipped

with a SQUID magnetometer (Quantum Design Company) and with a vibrating sample magnetometer (VSM) in a physical property measurement system PPMS 6000 (Quantum Design Company). The time dependence of the magnetization was measured at 6 T in the temperature range between 21 and 30 K for $\text{Sr}_3\text{CoIrO}_6$ and between 12.5 and 14 K for $\text{Sr}_3\text{NiIrO}_6$.

Magnetization measurements in pulsed magnetic fields were performed at the Dresden High Magnetic Field Laboratory (Forschungszentrum Dresden-Rossendorf) using a pulsed magnet powered by a 1.44 MJ capacitor bank.²⁰ With an inner bore of 20 mm, the magnet yielded fields up to 60 T with a rise time of 7 ms and a total pulse duration of about 20 ms. All measurements were performed twice, with and without the sample, in order to remove the background signal contribution. All the data were collected at a temperature of 50 K.

D. Low-temperature synchrotron powder diffraction

The crystal structures of $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$ in the temperature range of 9–300 K were determined by synchrotron powder diffraction at the beamline B2²¹ at HASYLAB/DESY (Hamburg, Germany). The investigations were performed in a quartz capillary in a He atmosphere in Debye–Scherrer mode using the onsite readable image-plate detector OBI²² and a He closed-cycle cryostat. The synchrotron x-ray wavelengths used for each sample were 0.53837 Å ($\text{Sr}_3\text{CoIrO}_6$) and 0.53922 Å ($\text{Sr}_3\text{NiIrO}_6$).

E. Low-temperature neutron powder diffraction

Elastic coherent neutron scattering experiments were performed in zero field on the high-resolution structure powder diffractometer (SPODI) at the research reactor FRM-II (Garching, Germany) with monochromatic neutrons of 1.5481(1) Å wavelength.²³ Measurements were performed in Debye–Scherrer geometry. The powder sample (*ca.* 1 cm³ in volume) was filled into a thin-wall (0.15 mm) vanadium can of 10-mm diameter and then mounted in a top-loading closed-cycle refrigerator, which was cooled down from room temperature to 4 K in five hours. Helium 4 was used as a heat transmitter. The temperature was measured using two Cernox thin-film resistance cryogenic temperature sensors and controlled by a temperature controller from LakeShore. Powder diffraction data were collected between 4 and 70 K and then corrected for geometrical aberrations and the curvature of the Debye–Scherrer rings. The collecting time for a typical diffraction pattern was five hours.

Experiments with polarized neutrons have been carried out with the DNS spectrometer (Jülich Centre for Neutron Science [JCNS], FRM-II reactor). An unambiguous separation of nuclear coherent, spin incoherent, and magnetic scattering contributions over a wide scattering angle has been achieved by neutron polarization analysis applying the well-established *xyz* method.²⁴ The experiment was carried out at two temperatures, 4 and 80 K, using monochromatic neutrons with a wavelength of 4.74 Å. The polarization of the neutron beam was better than 96%.

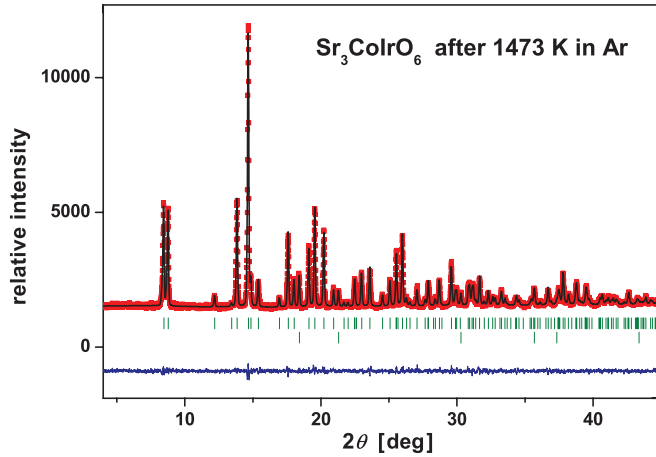


FIG. 1. (Color online) Room temperature x-ray diffraction pattern of $\text{Sr}_3\text{CoIrO}_6$, prepared at 1473 K in an Ar atmosphere, observed, and calculated profiles, based on the Rietveld refinement of a structure model derived from the K_4CdCl_6 structure, together with their difference curve. Tick marks represent, from top to bottom, the positions of reflections for $\text{Sr}_3\text{CoIrO}_6$ [$R\text{-}3c$, $a = 9.62112(9)$ Å, $c = 11.1541(1)$ Å] and metallic Ir ($Fm\text{-}3m$, 1% w/w).

F. Heat capacity

The heat capacity was measured between 10 and 150 K for $\text{Sr}_3\text{CoIrO}_6$ and between 4 and 250 K for $\text{Sr}_3\text{NiIrO}_6$ in zero magnetic field with a standard puck in a PPMS (Quantum Design) applying the relaxation method with 2% temperature rise.

III. RESULTS AND DISCUSSION

A. Crystal structures of Sr_3MIrO_6 ($M = \text{Co}, \text{Ni}$)

The XRD pattern of $\text{Sr}_3\text{CoIrO}_6$ and a Rietveld refinement is presented in Fig. 1. The Sr_3MIrO_6 structure contains one-dimensional chains along the c direction consisting of alternating face-sharing MO_6 trigonal prisms and IrO_6 octahedra (Fig. 2). The chains are separated by Sr cations. Each Co-Ir chain is shifted relatively to three nearest-neighbor chains by $z = 1/3$ and relatively to the other nearest-neighbor chains by $z = 2/3$ (Fig. 2). This means that the phase of each chain is shifted relatively to three nearest-neighbor chains by 60° and to the other three nearest-neighbor chains by 120° toward the c axis. The lattice parameters are $a = 9.62112(9)$ Å and

$c = 11.1541(1)$ Å. The intrachain Co-Co distance in $\text{Sr}_3\text{CoIrO}_6$ is 5.577 Å and between the chains is 5.857 Å. $\text{Sr}_3\text{NiIrO}_6$ is isostructural to $\text{Sr}_3\text{CoIrO}_6$ with the lattice parameters $a = 9.6188(2)$ Å, $c = 11.2004(3)$ Å, the intrachain Ni-Ni distance of 5.600 Å, and the interchain distance of 5.859 Å (XRD data are not shown).

In contrast to the $\text{Ca}_3\text{Co}_{1+x}\text{Ir}_{1-x}\text{O}_6$ -system,⁹ in which the whole series from $x(\text{Co}) = 0$ to $x(\text{Co}) = 1$ exists, attempts to synthesize $\text{Sr}_3\text{Co}_{1.5}\text{Ir}_{0.5}\text{O}_6$ led to a mixture of (i) $\text{Sr}_3\text{Co}_{2-x}\text{Ir}_x\text{O}_6$ [$R\text{-}3c$, $a = 9.6149(3)$ Å, $c = 11.1370(5)$ Å]; (ii) cubic $\text{Sr}_2\text{Co}_{1-x}\text{Ir}_x\text{O}_6$ with a perovskite-type structure [$Fm\text{-}3m$, $a = 7.8351(2)$ Å]; and (iii) a small amount of metallic Ir. Some differences in lattice parameters of isostructural $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{Co}_{2-x}\text{Ir}_x\text{O}_6$ enabled us to propose a small Co/Ir nonstoichiometry in our samples. A slight occupancy of Co on the respective Ir site (less than 3%) was also found by a Rietveld refinement of $\text{Sr}_3\text{CoIrO}_6$ and explains the presence of metallic Ir impurities (less than 1% w/w) in the sample. Note that a significant cation mixing can cause a huge change in the magnetic behavior, as found for the closely related $\text{Sr}_3\text{ZnRhO}_6$. In fact, $\text{Sr}_3\text{ZnRhO}_6$ with a commensurate crystal structure presents a clear long-range magnetic ordering at 16 K, as confirmed by heat capacity and neutron powder diffraction measurements.²⁵ On the other hand, the compound of the same composition with an incommensurate crystal structure and the mixed occupancy of octahedral and prismatic sites by Zn, Rh, and Sr cations shows a Curie-Weiss-like behavior down to 2 K.²⁶

B. X-ray absorption spectroscopy study of $\text{Sr}_3\text{CoIrO}_6$

In order to determine the valence of Ir in $\text{Sr}_3\text{CoIrO}_6$ we performed Ir- L_{III} XAS investigations of $\text{Sr}_3\text{CoIrO}_6$ together with isostructural $\text{Sr}_3\text{ZnIrO}_6$ as a reference compound for Ir^{4+} .

It is well known that the white line position in the Ir- L_{III} edge is shifted to higher energy by more than one eV with an increase in the formal valence of Ir ion from $3+$ to $4+$.^{27,28} In Fig. 3 we compare the Ir- L_{III} absorption spectra of $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{ZnIrO}_6$. Since the white line position of both compounds lies at the same energy, the existence of an $\text{Ir}^{4+}/\text{Co}^{2+}$ valence state can be inferred. Moreover, the very similar near-edge spectral structures indicate the same local environment for both materials. Note that the existence of Ir^{3+} in complex oxides is rather unlikely and has only been mentioned for Sr_2MIrO_6 ($M = \text{Nb}, \text{Ta}$) perovskites.²⁹

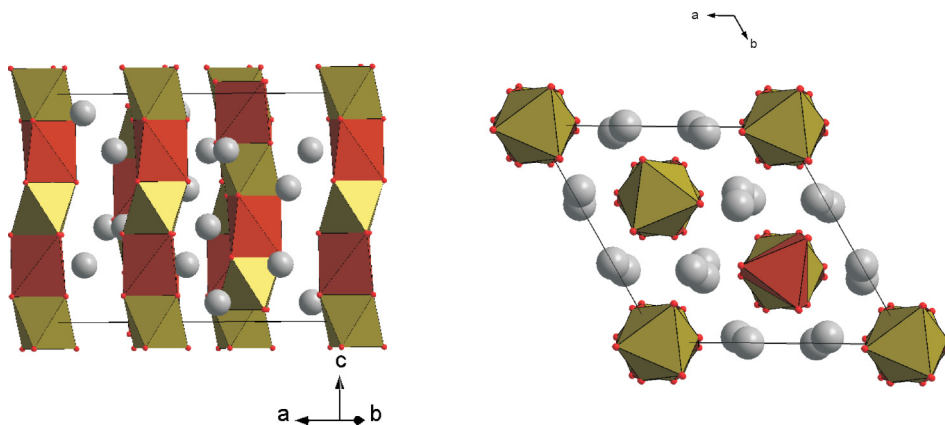


FIG. 2. (Color online) Crystal structure of $\text{Sr}_3\text{CoIrO}_6$ presenting one-dimensional chains along the c direction consisting of alternating face-sharing CoO_6 trigonal prisms and IrO_6 octahedra (left). Grey spheres are Sr atoms. A projection of one unit cell on the ab plane is shown (right).

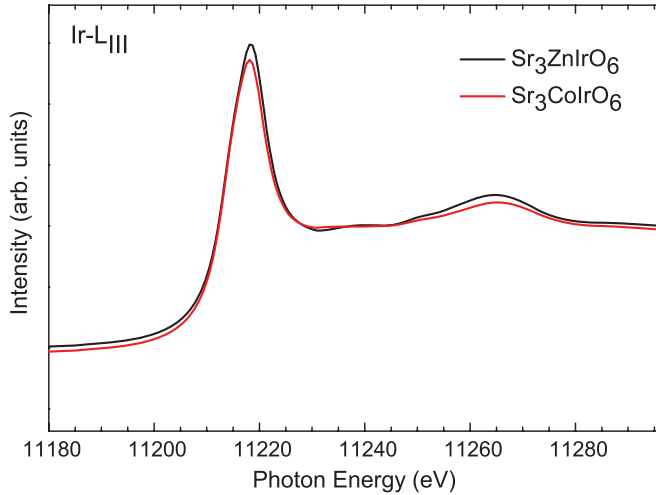


FIG. 3. (Color online) Ir L_{III} -edge XAS in the white line region, for $\text{Sr}_3\text{ZnIrO}_6$ as a standard for Ir^{4+} (black line) and $\text{Sr}_3\text{CoIrO}_6$ (red/dark gray line).

C. Magnetic characterization

1. Temperature dependence of magnetization

The temperature dependences of the magnetization for $M = \text{Co}$ and Ni in an external magnetic field of 0.05 T are similar [see Fig. 4(a)]. A significant difference between FC and ZFC measurements points to the appearance of a ferro- or ferrimagnetic component at low temperature. For each phase, two characteristic temperatures, $T_1 = 90$ K and $T_2 = 25$ K for Co, and $T_1 = 85$ K and $T_2 = 15$ K for Ni (see inset in Fig. 4), are observed. Below T_1 a significant increase of magnetization can be seen, and below T_2 a weak temperature dependence of magnetization in the FC and practically zero magnetization values in ZFC mode were detected. The same two characteristic temperatures were also observed in the significantly smaller magnetic field of 0.005 T (data not shown here). While for $\text{Ca}_3\text{CoRhO}_6$ two characteristic temperatures $T_1 = 90$ K and $T_2 = 30$ K were observed, only one temperature corresponding to the onset of a large difference between FC and ZFC was detected for $\text{Ca}_3\text{CoIrO}_6$.¹⁰

For $\text{Sr}_3\text{NiIrO}_6$ we observe a spin-freezing temperature $T_2 \sim 15$ K (Fig. 4), which is similar to the results reported in Refs. 12 and 19. The authors of Ref. 12 have discussed the magnetic behavior of $\text{Sr}_3\text{NiIrO}_6$ in low magnetic fields between T_1 and T_2 as a PDA state, corresponding to the coexistence of 2/3 antiferromagnetically coupled ferrimagnetic chains with antiferromagnetic intrachain coupling between Ni^{2+} ($S = 1$) and Ir^{4+} ($S = \frac{1}{2}$) and 1/3 magnetically incoherent chains in a triangular lattice. However, it has to be noted that in the neutron diffraction pattern no evidence for antiferromagnetic order could be seen.¹⁹ Antiferromagnetic coupling between Ni^{2+} and Ir^{4+} was postulated based (i) on the negative Curie–Weiss temperature in the paramagnetic region, (ii) low magnetization values and the absence of saturation even in the field of 35 T,¹² and (iii) supported by theoretical calculations.¹³

We analyzed the temperature dependence of the reciprocal molar magnetic susceptibility of $\text{Sr}_3\text{NiIrO}_6$ in the paramagnetic region above 200 K applying a Curie–Weiss law Eq. (1) and found a paramagnetic moment of $3.50(1) \mu_B$ per f.u. The

Curie–Weiss temperature $\theta = -33(5)$ K indicates a dominant antiferromagnetic interaction [Fig. 4(b)],

$$\frac{1}{\chi(T)} = \frac{3k_B(T - \theta)}{\mu_{\text{eff}}^2} = \frac{1}{\chi_0(T)} - \lambda. \quad (1)$$

In contrast to $\text{Sr}_3\text{NiIrO}_6$, our magnetization data of $\text{Sr}_3\text{CoIrO}_6$, fitted by the Curie–Weiss equation Eq. (1) between 250 and 400 K, revealed a positive Curie–Weiss temperature $\theta = 178(3)$ K and a paramagnetic moment of $4.36(1) \mu_B$ per f.u.

Here we would like to make a note of caution. In principle, one has to be careful in applying the equation Eq. (1) for analyzing the paramagnetic susceptibility and drawing conclusions about the magnitude of magnetic moments and interactions in Co^{2+} -containing materials.^{15–17,30} the degeneracy of the crystal field split states of a d^7 configuration may be lifted by the spin-orbit interaction, leading to nontrivial temperature dependence of the magnetic susceptibility. To what extent this is the case for $\text{Sr}_3\text{CoIrO}_6$ will be subject of a further study looking into the details of the electronic structure of this material.

2. Field dependence of magnetization

The field dependence of the magnetization of Sr_3MIrO_6 was systematically investigated between 10 and 90 K for $M = \text{Co}$ and between 5 and 55 K for $M = \text{Ni}$ with steps of 10 K. Each hysteresis curve was started and finished at 9 T for $M = \text{Co}$ and 6 T for $M = \text{Ni}$. After each measurement the field was switched off, and the sample was heated to the paramagnetic state above 100 K and cooled down without field to the next temperature. For $\text{Sr}_3\text{CoIrO}_6$ a saturation in the magnetization value of about $2.2 \mu_B/\text{f.u.}$ was observed above 4 T for temperatures between 30 and 90 K (Fig. 5). Below 60 K an additional plateau at about $0.7 \mu_B$ located between 0.5 and 1.8 T becomes visible. Below 30 K a quite different behavior without any saturation was observed (see Fig. 5).

Completely different magnetic hysteresis curves at 15 K for $\text{Sr}_3\text{CoIrO}_6$ were observed (Fig. 6) depending on whether the sample was cooled down without or with applied magnetic field. No saturation behavior and zero hysteresis loop was observed for the state after cooling down in zero field, while a hysteresis with saturated magnetization values, asymmetrically extended with respect to the magnetization axis, has been seen after cooling down in a magnetic field of 1 T. This difference in the magnetic behavior reflects the slow-spin dynamics below 25 K for $\text{Sr}_3\text{CoIrO}_6$ and resembles the frozen F-PDA state of $\text{Ca}_3\text{CoRhO}_6$.^{3–5}

Applying pulsed magnetic fields up to 60 T at 50 K led also to a magnetic saturation with $2.2 \mu_B/\text{f.u.}$ (see Fig. 7). Note that an almost saturated magnetization of $4.05 \mu_B/\text{f.u.}$ parallel to the c axis was observed for the $\text{Ca}_3\text{CoRhO}_6$ polycrystalline sample, field-oriented along the c axis at ~ 19 T and 70 K.³ Due to strong magnetocrystalline anisotropy in such quasi-one-dimensional systems, the magnetization perpendicular to the easy c axis in $\text{Ca}_3\text{CoRhO}_6$ is much lower ($0.53 \mu_B/\text{f.u.}$ at ~ 19 T and 70 K) and not saturated.³ For a disordered $\text{Sr}_3\text{CoIrO}_6$ sample with random distribution of crystallites we can assume that about 1/3 of all

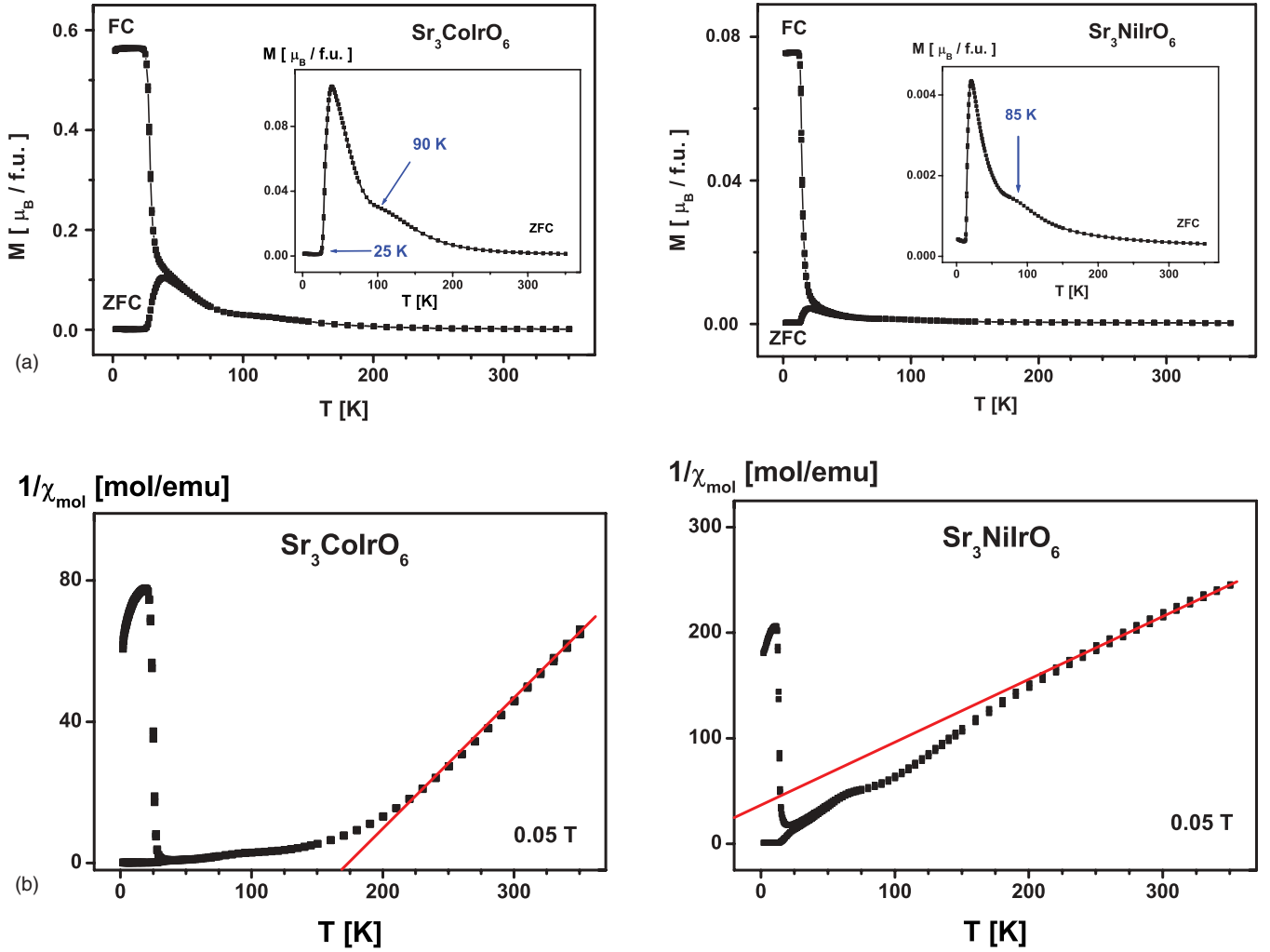


FIG. 4. (Color online) (a) Temperature dependence of magnetization at 0.05 T for $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$. A significant increase of magnetization below $T_1 = 90$ K for the Co phase and below $T_1 = 85$ K for the Ni phase was observed, see inset. In FC mode the samples were cooled down in a magnetic field of 0.1 T and measured at 0.05 T. (b) Temperature dependence of reciprocal molar magnetic susceptibility at 0.05 T for $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$. The drawn lines correspond to Curie-Weiss fits to the paramagnetic regions.

crystallites are oriented with the c axis along the magnetic field and deliver the largest contribution to the magnetization below the phase transition temperature. The plateau in magnetization between 0.5 and 1.8 T at 50 K will then correspond to $\sim 2.1 \mu_B/\text{f.u.}$, and the saturation above 4 T to $\sim 6.6 \mu_B/\text{f.u.}$ for a single crystal oriented along the easy c axis. A spin-only model would lead to a magnetization of $4 \mu_B/\text{f.u.}$ only: $M/\mu_B = 2^* (S_{\text{Co(II)}} + S_{\text{Ir(IV)}})$ with $S_{\text{Co(II)}} = 3/2$ and $S_{\text{Ir(IV)}} = 1/2$. The $6.6 \mu_B$ value therefore indicates that the Co^{2+} ions must carry a significant orbital moment, well in line with the strong magnetocrystalline anisotropy. The plateau between 0.5 and 1.8 T could correspond to the ferrimagnetic ordering of Ir^{4+} and Co^{2+} ions, where $2/3$ of the magnetic chains have all the spins parallel to the magnetic field and the other $1/3$ has all the spins antiparallel.

The observed hysteresis in the magnetization up to 15 T (Fig. 7) in pulsed magnetic fields is probably due to the slow kinetics of spin orientations. Note that the measured magnetization of disordered $\text{Ca}_3\text{CoRhO}_6$ polycrystalline sample is far from the saturation.³¹

For our disordered polycrystalline sample of $\text{Sr}_3\text{NiIrO}_6$, a tendency for a plateau in the magnetization with $\sim 0.2 \mu_B/\text{f.u.}$ can be seen at 15 K for fields above 5 T. At higher temperatures this tendency disappears completely (see Fig. 8). A coercive field of $\mu_0 H = 0.25$ T was determined at 15 K. Below 15 K a more linear behavior with much smaller magnetization values without a significant coercivity were observed. At 15 K, a plateau at 5 T with a magnetization of $0.15 \mu_B/\text{f.u.}$ in static magnetic field was reported in Ref. 12.

Assuming a magnetocrystalline anisotropy also for $\text{Sr}_3\text{NiIrO}_6$, we expect from our experiment a magnetization value of about $\sim 0.6 \mu_B/\text{f.u.}$ at 15 K for a single crystal sample oriented along the c axis. The magnetization value for antiferromagnetic alignment of Ni^{2+} and Ir^{4+} ions in the chains, which was proposed in the work¹³ based on density functional theory calculations, would be of $1.0 \mu_B/\text{f.u.}$ considering only spin contributions: $M = 2[1/3(S_{\text{Ni(II)}} - S_{\text{Ir(IV)}}) + 1/3(S_{\text{Ni(II)}} - S_{\text{Ir(IV)}}) + 1/3(S_{\text{Ni(II)}} - S_{\text{Ir(IV)}})]$ with $S_{\text{Ni(II)}} = 1$ and $S_{\text{Ir(IV)}} = 1/2$.

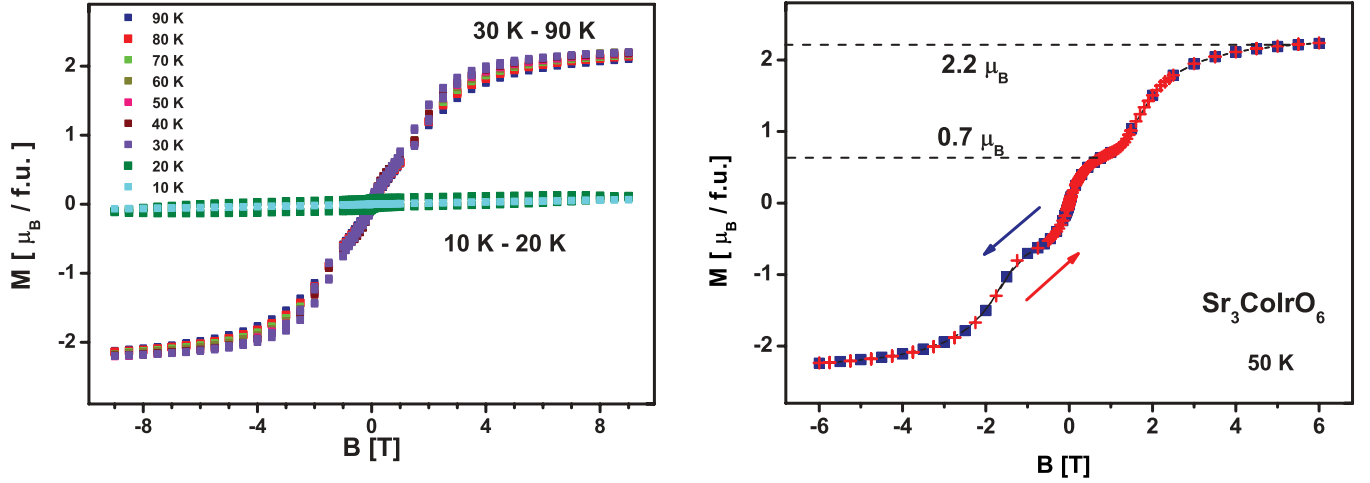


FIG. 5. (Color online) Field dependence of magnetization of $\text{Sr}_3\text{CoIrO}_6$ in the temperature range between 10 and 90 K (left) and at 50 K (right).

3. Time-dependent magnetic alignment in $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$

Below T_2 , the temperature of spin freezing at magnetic fields lower than 1 T, a frozen PDA state (F-PDA) with very slow dynamics of spins was discussed: $T_2 \sim 30$ K for $\text{Ca}_3\text{CoRhO}_6$,⁴ $T_2 = 25$ K for $\text{Sr}_3\text{CoIrO}_6$, and 15 K for $\text{Sr}_3\text{NiIrO}_6$ (present work or 21 K¹²). Increasing temperature and magnetic field leads to magnetic phase transitions into ferri- or ferromagnetic states,^{3,12} which are accompanied by the parallel orientation of spins inside individual domains and the movement of domain walls within the material. In a constant external magnetic field this domain switching is thermally activated and can be studied by measuring the magnetization as a function of time at temperatures close to T_2 .

The numerous isothermal material transformations during a time interval t can be described in terms of nucleation and growth rates by the Johnson–Mehl–Avrami–Kolmogorov

(JMAK) theory, for example see Ref. 32,

$$\alpha = 1 - \exp(-kt^n), \quad \text{or} \quad \ln[-\ln(1 - \alpha)] = \ln k + n \ln t. \quad (2)$$

Here α is the fraction of the already transformed material (or in our case already aligned domains in the material), k is the growth rate constant, and n is an integer or half integer. Thus, from the time dependence of the magnetization (measured at constant temperature T and magnetic field B), one can estimate the rate constant k of spin ordering during a magnetic phase transition. Moreover, from the temperature dependence of the growth rate $k = k(T)$, the activation energy E_a for domain switching can be calculated by applying the Arrhenius equation $k = k_0 \exp(-E_a/RT)$.

Magnetization as a function of time was measured for $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$ at fixed temperatures in an applied magnetic field of 6 T (Fig. 9). After each measurement at a given temperature the field was switched off, and the material was heated up to 70 K for $M = \text{Co}$ and up to 120 K for

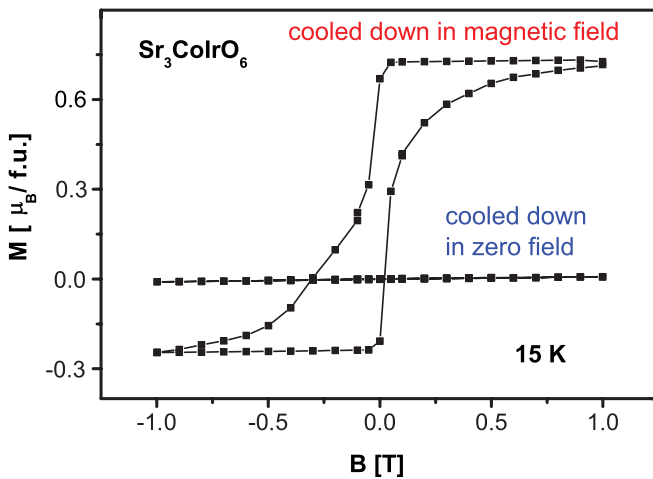


FIG. 6. (Color online) Field dependence of magnetization at 15 K for $\text{Sr}_3\text{CoIrO}_6$ cooled down without magnetic field and cooled down in magnetic field of 1 T.

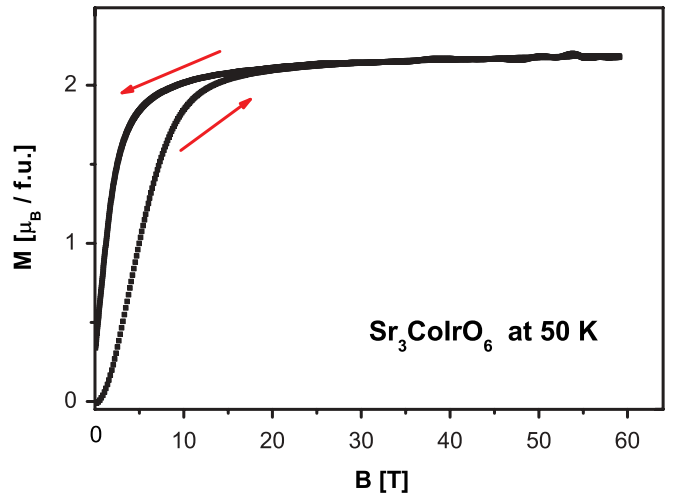
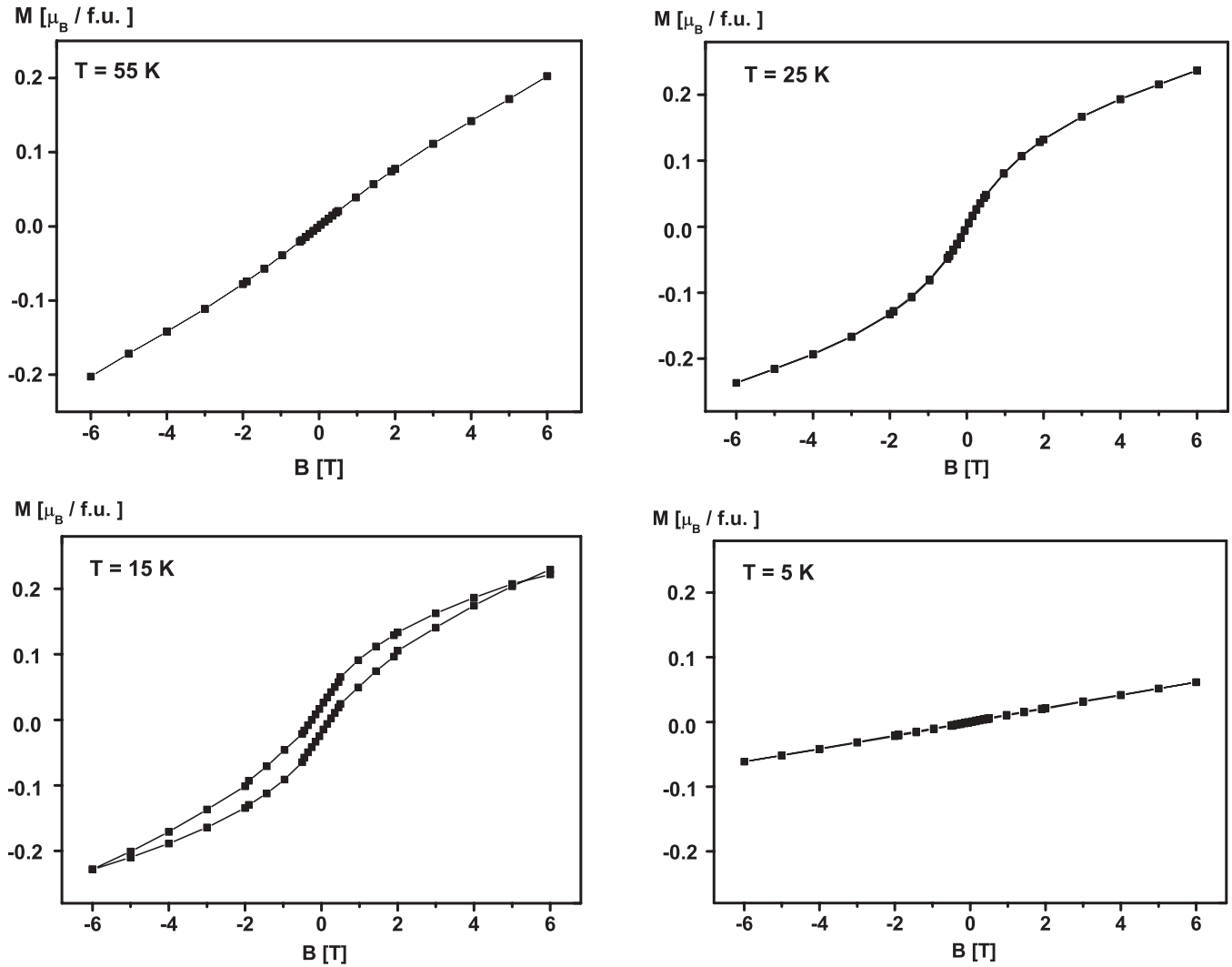


FIG. 7. (Color online) Magnetization curves of $\text{Sr}_3\text{CoIrO}_6$ at 50 K in pulsed magnetic fields up to 60 T. A significant hysteresis below 15 T is probably due to the slow kinetics of the reorientation of spins during the magnetic field pulses.

FIG. 8. Field dependence of the magnetization for polycrystalline $\text{Sr}_3\text{NiIrO}_6$ at temperatures 5–55 K.

$M = \text{Ni}$, in order to disorder the magnetic domains, and then cooled down to the next temperature. A saturated

magnetization $M_s = 2.2 \mu_B/\text{f.u.}$ for the Co system and $M_s = 0.216 \mu_B/\text{f.u.}$ for the Ni system were used for the calculation

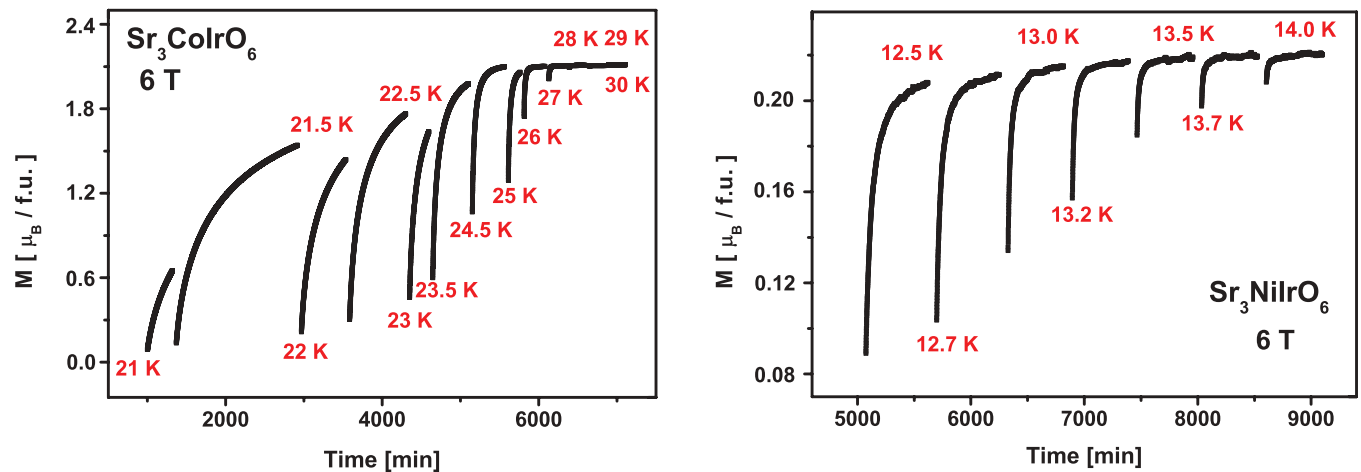


FIG. 9. (Color online) Magnetizations of $\text{Sr}_3\text{MCoIrO}_6$, $M = \text{Co}$ (left) or Ni (right) as a function of time at different temperatures in an applied magnetic field of 6 T. The magnetic domain structure was reset to the virgin state for each temperature by annealing the system in zero field at temperatures in the paramagnetic region.

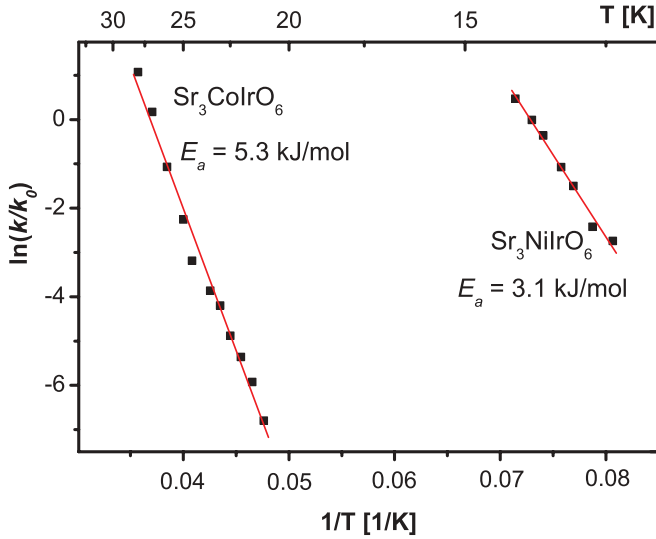


FIG. 10. (Color online) Arrhenius plot for spin ordering in $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$ with k_0 [sec⁻¹] for $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$.

of $\alpha(t) = M(t)/M_s$, the fraction of the already aligned domains in the sample as a function of time t . For each temperature the magnetization data were fitted by Eq. (2), and $\ln(k)$ was extracted from the linear region with n values between 0.2 and 0.6. The activation energy estimated from the Arrhenius plot for the alignment of the magnetic domains is about 5.3(3) kJ/mol, or 0.055 eV/f.u. for $\text{Sr}_3\text{CoIrO}_6$, and about 3.1(2) kJ/mol, or 0.032 eV/f.u. for $\text{Sr}_3\text{NiIrO}_6$ (Fig. 10).

4. Low-temperature synchrotron diffraction studies

The temperature dependences of the unit cell parameters of $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$ are influenced by the magnetic order and, therefore, reflect the complicated magnetic behavior (see Fig. 11). Some line broadening of reflections with decreasing temperature was observed, pointing out a probable formation

of local regions with a slightly distorted structure in the material. The thermal expansion coefficients for the a and c directions are positive and almost constant in the temperature region from room temperature down to the antiferromagnetic ordering temperature of about 100 K. This phonon part of the thermal expansion along a and c was estimated by a Debye function³³ with a Debye temperature for both compounds of about 300 K. For the fit modules of the McPhase modeling suite were used,³⁴ and only data points with $T > 100$ K were taken into account. Below this temperature the spontaneous magnetostriction leads to a zero-expansion behavior or even negative thermal expansion for both a and c for $\text{Sr}_3\text{CoIrO}_6$, whereas the spontaneous magnetostriction is much smaller for c in $\text{Sr}_3\text{NiIrO}_6$. Because of the likely large orbital moment of Co, the spontaneous magnetostriction³³ and the crystal field influence on the thermal expansion³⁵ of $\text{Sr}_3\text{CoIrO}_6$ is expected to be larger than in $\text{Sr}_3\text{NiIrO}_6$.

5. Heat-capacity study of the magnetic order in $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$

Temperature-dependent specific heat data for $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$ (Fig. 12) are monotonous, without any indication for a lambda peak, which would be expected for the onset of the long-range magnetic order. A λ peak at the magnetic transition temperature was not detected for $\text{Ca}_3\text{CoRhO}_6$, although a well-defined λ peak has been observed for the isostructural $\text{Ca}_3\text{Co}_2\text{O}_6$.⁸ The application of an external magnetic field of 2 T does not change the heat capacity of $\text{Ca}_3\text{CoRhO}_6$ at temperatures close to the paramagnetic-to-ferrimagnetic transition.⁸

D. Neutron diffraction study of $\text{Sr}_3\text{CoIrO}_6$

1. Unpolarized neutrons

The magnetic structure of $\text{Sr}_3\text{CoIrO}_6$ was determined from neutron powder diffraction at 4 K (Table I).

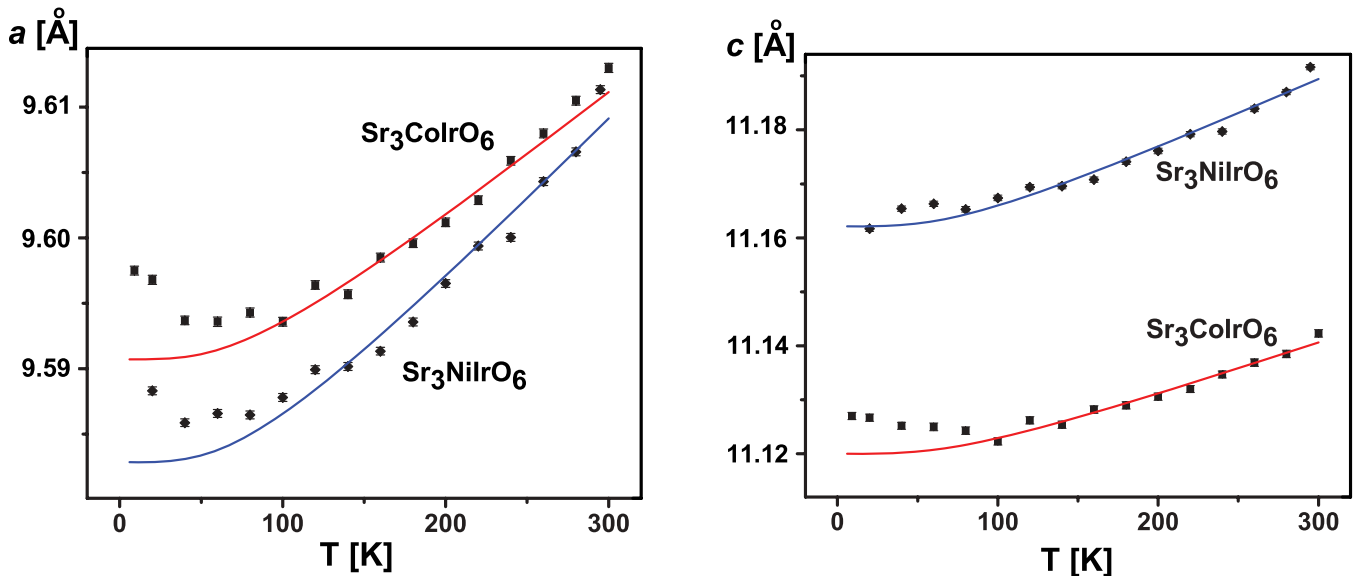
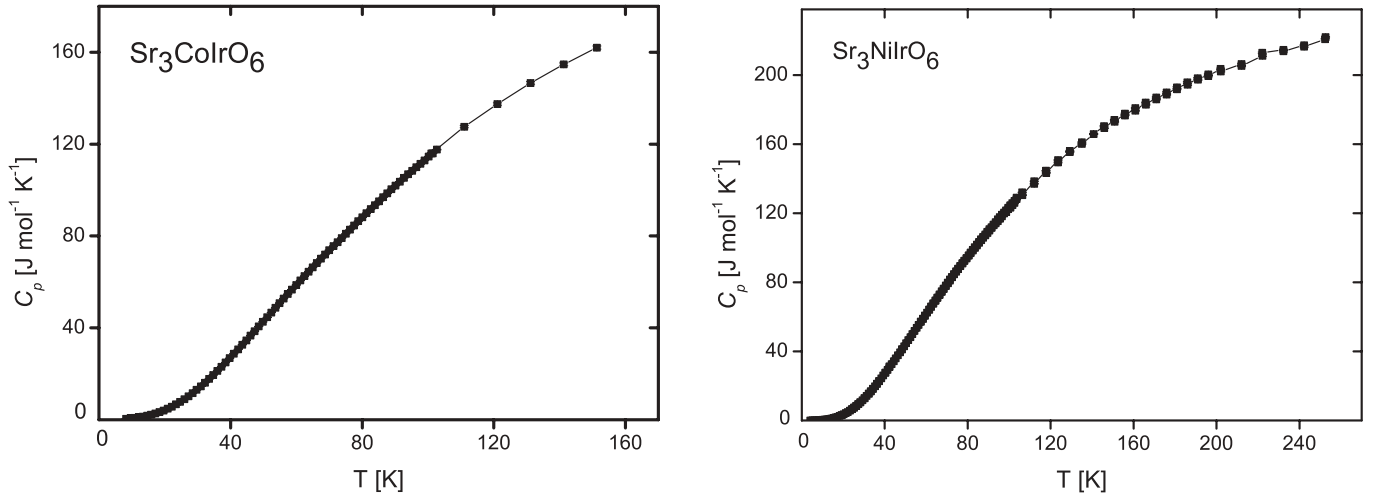


FIG. 11. (Color online) Temperature evolution of the lattice parameters of $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$. Lines indicate a Debye function, which is used to model the phonon part of the thermal expansion.

FIG. 12. Specific heat of $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$ in zero magnetic field as a function of temperature.

No changes in the diffraction pattern were detected between 300 and 73 K, while below 73 K additional reflections with the most intense one at 2θ of about 10.5° were observed (see Fig. 13). The intensity of this magnetic reflection does not change with decreasing temperature below 36 K. Note that the full width at half maximum (FWHM) parameter for magnetic reflections is much larger than that for nuclear reflections (Fig. 14), indicating short-range order in the material. A neutron powder diffraction study of the related $\text{Ca}_3\text{CoRhO}_6$ compound showed additional broad diffuse magnetic intensity at the strongest magnetic Bragg reflection.⁶ This effect was interpreted as the coexistence of long-range and short-

range magnetic ordering in the material. For $\text{Sr}_3\text{NiIrO}_6$, no magnetic reflections were identified in the neutron diffraction pattern at 10 K by comparison to the pattern at 300 K.¹⁹

All diffraction patterns have been analyzed by full-profile Rietveld refinements using the software package FullProf.³⁶ In order to eliminate the correlation between Co and Ir thermal displacement parameters B and the magnitude of magnetic moments at 4 K, the structural model was refined with fixed values $B(\text{Co})$ of 0.1 \AA^2 and $B(\text{Ir})$ of 0.2 \AA^2 (Table I). The mixed occupancy Ir/Co on the $6b$ site was also fixed to 0.97/0.03 values at 4 K.

TABLE I. Structural parameters for $\text{Sr}_3\text{CoIrO}_6$ at 270 K and 4 K as refined based on neutron powder diffraction data. A small excess of Co in the structure relative to Ir was revealed and quantified by 3% of Co on the Ir site. The magnetic space group for the magnetic structure was $R\bar{3}$.

| | $\text{Sr}_3\text{CoIrO}_6$, 270 K $R\bar{3}c$ | $\text{Sr}_3\text{CoIrO}_6$, 4 K $R\bar{3}c$ |
|---------------------------------|--|--|
| Space group | | |
| a (Å), c (Å) | 9.61981(7), 11.1578(2) | 9.59759(9), 11.1384(2) |
| V (Å ³) | 894.22(2) | 888.54(2) |
| Z | 6 | 6 |
| Sr | 18e | 18e |
| (x, y, z) | [0.3636(1), 0, 0.25] | [0.3638(1), 0, 0.25] |
| B (Å ²) | 0.56(3) | 0.20(2) |
| Co | 6a | 6a |
| (x, y, z) | (0, 0, 0.25) | (0, 0, 0.25) |
| B (Å ²) | 0.30(9) | 0.10 |
| Ir/Co 0.97(1)/0.03(1) | 6b | 6b |
| (x, y, z) | (0, 0, 0) | (0, 0, 0) |
| B (Å ²) | 0.20(4) | 0.20 |
| O | 36f | 36f |
| (x, y, z) | [0.1727(1), 0.0203(1), 0.1132(1)] | [0.1724(1), 0.0203(1), 0.1134(1)] |
| B (Å ²) | 0.66(3) | 0.32(2) |
| Co–O (Å) | 2.1916(13) | 2.1828(10) |
| Ir(Co)–O (Å) | 2.0170(13) | 2.0100(8) |
| $M_z(\text{Co}^{2+})$, μ_B | – | 3.6(1) |
| $M_z(\text{Ir}^{4+})$, μ_B | – | –0.6(2) |
| Bragg R factor, % | 3.17 | 4.22 |
| R_f factor, % | 1.81 | 2.57 |

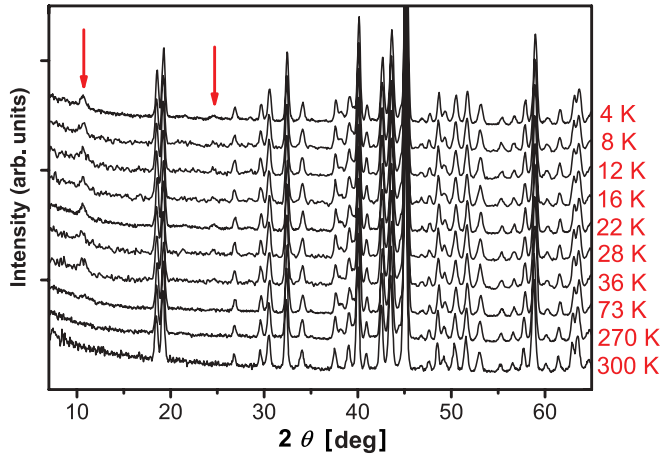


FIG. 13. (Color online) Temperature evolution of a section of the neutron diffraction patterns of $\text{Sr}_3\text{CoIrO}_6$ ($\lambda = 1.548 \text{ \AA}$).

Three different models for the magnetic structure in zero magnetic field were discussed in literature for the isostructural

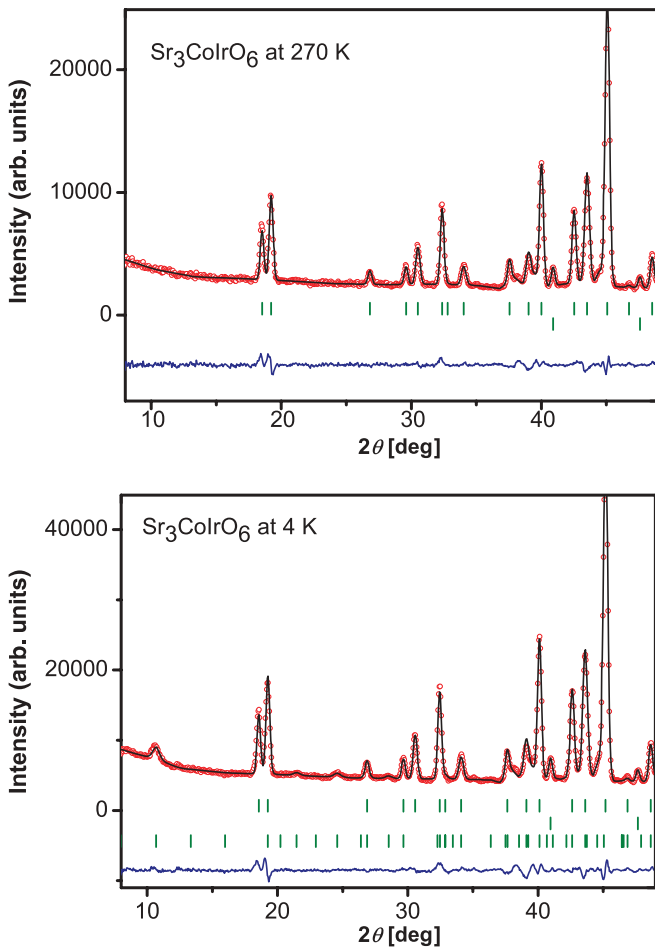


FIG. 14. (Color online) Sections of the neutron diffraction patterns of $\text{Sr}_3\text{CoIrO}_6$ at 270 K and 4 K (lower 2θ region). The positions of the magnetic Bragg reflections at 4 K are shown by the lower line of marks for the “ $+M, -M/2, -M/2$ ” structure model. The other marks indicate the Bragg reflections from the crystal structure (top) and 0.8% (w/w) Ir (middle).

$\text{Ca}_3\text{Co}_2\text{O}_6$ and $\text{Ca}_3\text{CoRhO}_6$ compounds: (i) an incommensurate amplitude modulated antiferromagnet²; (ii) the PDA,^{3,4} where 2/3 of magnetic chains order antiferromagnetically and the other 1/3 are disordered; and (iii) a ferrimagnetic structure with 2/3 of the magnetic chains ferromagnetically and the other 1/3 antiferromagnetically aligned.¹ In addition, the short-range magnetic order of Co^{2+} ions, as revealed by the diffuse character of the magnetic 100 reflection, was proposed.⁶ It is an extremely difficult task to draw unambiguous conclusions from a powder diffraction pattern in these kinds of systems. This is demonstrated by the highly complex modulated PDA structure with a very long periodicity, which was revealed for $\text{Ca}_3\text{Co}_2\text{O}_6$ based on high-resolution magnetic x-ray scattering.³⁷

A ferrimagnetic order of the interchain spin arrangement in the ab plane can be ruled out for $\text{Sr}_3\text{CoIrO}_6$, because no significant change of intensity of the nuclear reflections is observed below the magnetic transition. This is consistent with the very low moment seen in the ZFC magnetization data [Fig. 4(a)]. A Rietveld refinement of the nuclear structure confirms that the Ir- and Co-ions are located on octahedral and trigonal-prismatic coordinated sites, respectively (Table I). Two different magnetic structure models were considered in order to explain the magnetic reflections below 73 K: (i) a commensurate modulated antiferromagnetic structure² with the propagation vector $\mathbf{k} = (0, 0, 1)$ in the space group $R\bar{3}$; and (ii) the PDA ($+M, -M, 0$) structure⁶ with the propagation vector $\mathbf{k} = (0, 0, 0)$ in the space group $P\bar{3}$.¹

An incommensurate modulated antiferromagnetic structure with propagation vector $\mathbf{k} = (0, 0, k_z)$ has been also considered. In fact $(0, 0, 1)$ is not a special point of the Brillouin zone, and a small incommensurate propagation vector $(0, 0, 1.01)$, corresponding to a very long modulation, was observed in $\text{Ca}_3\text{Co}_2\text{O}_6$.^{2,37} However, given the limited resolution of our powder diffraction data we can determine k_z to be $k_z = 1.00 \pm 0.01$ and therefore use $\mathbf{k} = (0, 0, 1)$ in the following discussion.

The magnetic form factor of iridium has been approximated by that of Rh.³⁸

Both magnetic models (i) and (ii) can excellently describe the magnetic reflections with nearly similar magnetic moments on the iridium site [$0.6(1)$ – $0.7(1) \mu_B/\text{f.u.}$] and cobalt site [$3.3(1)$ or $3.6(1) \mu_B/\text{f.u.}$] and very similar residuals at 4 K. The commensurate antiferromagnetic structure (i) with $\mathbf{k} = (0, 0, 1)$ is supported for $\text{Sr}_3\text{CoIrO}_6$ by the following three considerations: (1) a modulated antiferromagnetic structure with $R\bar{3}$ exhibits higher symmetry in comparison to the $P\bar{3}$ one of the PDA; (2) magnetizations in a low magnetic field above $T_2 = 30 \text{ K}$ are close to zero [see Fig. 4(a)], which is too low for a PDA state with 1/3 of the chains in the structure being randomly oriented; and (3) the critical magnetic field strength of 1 T for the first field-induced magnetic phase transition into a ferrimagnetic state at 50 K (see Fig. 5) seems too high for a spin reorientation in the incoherent magnetic chains of the PDA.

The magnetic structure has been analyzed using the standard irreducible representation theory for the propagation vector $\mathbf{k} = (0, 0, 1)$. Only the symmetry-adapted mode belonging to the irreducible representation Γ_1 allows a fit to the data. The magnetic moments for Co and Ir ions located at the $6a$ $(0, 0, 1/4)$ and $6b$ $(0, 0, 0)$ sites, respectively, are given by

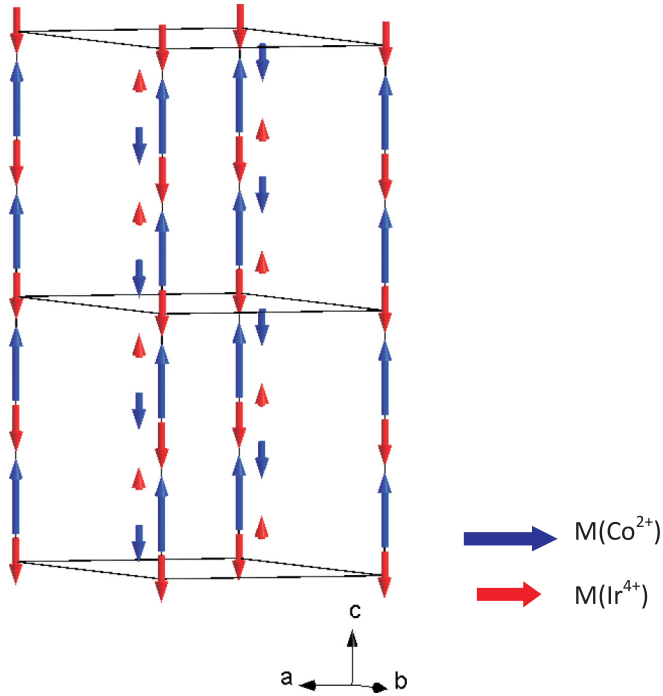


FIG. 15. (Color online) A commensurate, modulated antiferromagnetic structure of $\text{Sr}_3\text{CoIrO}_6$ with the propagation vector $\mathbf{k} = [0, 0, 1.00(1)]$. The arrangement of the ordered magnetic moments in the ab plane can be described as $(M, -M/2, -M/2)$.

$\mathbf{M}_{j=a,b}(\mathbf{R}_L) = \mathbf{M}_j \cos(2\pi \mathbf{k} \cdot \mathbf{R}_L)$. Here the Fourier coefficients \mathbf{M}_a and \mathbf{M}_b correspond to the maximum magnetic moments at the $6a$ and $6b$ sites, respectively, and \mathbf{R}_L is the translation vector with respect to the zeroth cell. All magnetic moments are aligned parallel to the c axis. Using the noninteger translations inside the magnetic unit cell $t_1 = (2/3, 1/3, 1/3)$ and $t_2 = (1/3, 2/3, 2/3)$, one can see that there is a phase shift of 120° in the magnetic moment between adjacent chains. Consequently, the arrangement of the ordered magnetic moments in the ab plane can be described as $(M, -M/2, -M/2)$, where the labels in parenthesis indicate the relative magnetizations on the triangular network formed by the chains. Note that the relevant phase factors are $\cos(2\pi/3) = \cos(4\pi/3) = -1/2$.

A scheme of the magnetic structure is shown in Fig. 15. This type of structure is usually induced by competing exchange

interactions in the presence of strong axial anisotropy, stabilizing an arrangement in which the ordered component of the magnetic moment fluctuates along the propagation direction. The refined values of the magnetic Co moment of $3.6(1) \mu_B$ and Ir moments of $-0.6(1) \mu_B$ do not depend significantly on temperature between 4 K and 36 K within the available resolution of the diffraction data.

The $3.6 \mu_B$ value for the Co^{2+} is larger than the spin-only value of $3 \mu_B$ for an $S = 3/2$ ion and indicates, therefore, the presence of orbital moment on the Co.

2. Polarized neutrons

Measured intensities recorded by diffraction with polarized neutrons are shown in Fig. 16. The nuclear contributions, as derived from the polarization analysis of data collected at 4 and 80 K, are very similar, indicating that no structural phase transition of $\text{Sr}_3\text{CoIrO}_6$ takes place in this temperature range. The nearly temperature-independent incoherent scattering increases nonlinear with Q and exhibits a maximum at $\sim 2.2 \text{ \AA}^{-1}$. The magnetic contribution at 4 K yields a clear peak at $Q = 0.75 \text{ \AA}^{-1}$, which is not visible at 80 K and should be related to the magnetic order in $\text{Sr}_3\text{CoIrO}_6$. Nevertheless, the shape of the magnetic contribution at 4 K and 80 K is far from linear, i.e., two broad maxima at 0.75 and 1.75 \AA^{-1} were observed, thus indicating the presence of a diffuse magnetic signal, probably due to short-range magnetic order above and below the magnetic ordering temperature, similar to $\text{Ca}_3\text{CoRhO}_6$.⁶

IV. CONCLUSION

We find that the magnetic behavior of $\text{Sr}_3\text{CoIrO}_6$ resembles more that of $\text{Ca}_3\text{CoRhO}_6$ with the same spin states of cations in MO_6 trigonal prisms and $\text{M}'\text{O}_6$ octahedra than that of $\text{Sr}_3\text{NiIrO}_6$ with Ni^{2+} ($S = 1$) and quenched orbital moment. All three compounds have two characteristic temperatures T_1 and T_2 , which separate spin freezing at very low temperature (below T_2) and an intermediate temperature region ($T_2 < T < T_1$) with field-induced magnetic transitions and the paramagnetic region at higher temperatures (above T_1). $\text{Sr}_3\text{CoIrO}_6$ shows nearly the same transition temperature $T_1 = 90 \text{ K}$ as $\text{Ca}_3\text{CoRhO}_6$, and the analysis of the inverse paramagnetic susceptibility indicates a similar size of the magnetic interactions in both compounds in spite of the larger Sr

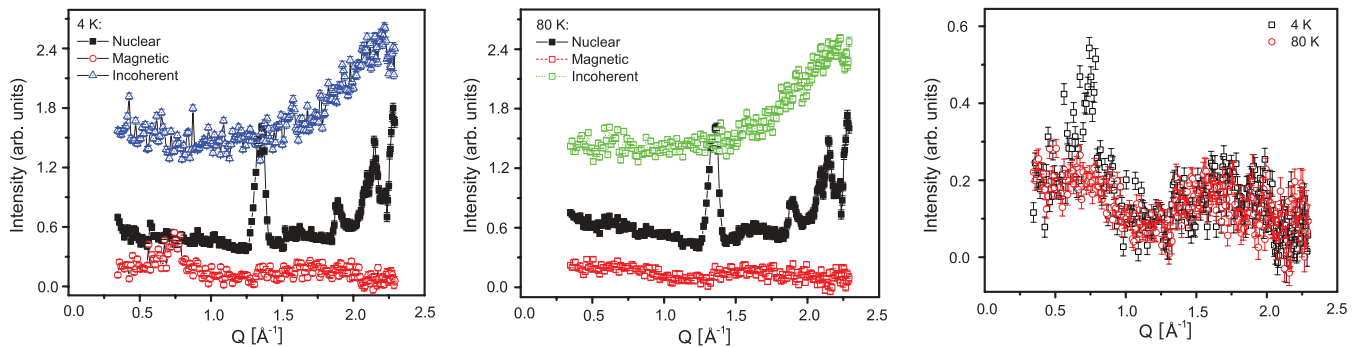


FIG. 16. (Color online) Different contributions to the diffraction patterns of $\text{Sr}_3\text{CoIrO}_6$ at (a) 4 K and (b) 80 K together with a comparison of the extracted magnetic contributions at (c) both temperatures.

atoms between the Co chains and, therefore, longer Co-Co interchain distances in $\text{Sr}_3\text{CoIrO}_6$. The complex magnetic order below the transition temperature T_1 influences the thermal behavior of the lattice parameters of $\text{Sr}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{NiIrO}_6$: both a and c parameters in $\text{Sr}_3\text{CoIrO}_6$ show pronounced magnetoelastic effects, whereas the spontaneous magnetostriction for c parameter in $\text{Sr}_3\text{NiIrO}_6$ is smaller.

Similar to $\text{Ca}_3\text{CoRhO}_6$, between T_1 and T_2 $\text{Sr}_3\text{CoIrO}_6$ seems to become purely ferromagnetic by a spin-flip transition at rather moderate external fields of 4–5 T. The magnetization of $\text{Sr}_3\text{NiIrO}_6$ is linear, and no saturation is observed in fields up to 7 T.

Powder neutron diffraction data of $\text{Sr}_3\text{CoIrO}_6$ and $\text{Ca}_3\text{CoRhO}_6$ in zero field can be interpreted successfully by either a pure antiferromagnetic or a PDA state. Below 100 K, neutron diffraction in an applied magnetic field of 2 T revealed a ferrimagnetic structure for $\text{Ca}_3\text{CoRhO}_6$,⁴ which corresponds to the first plateau in the field dependence of magnetization. A similar ferrimagnetic structure could be expected for $\text{Sr}_3\text{CoIrO}_6$, showing also a plateau at 50 K and about 1 T. Magnetic Bragg reflections were not observed in the neutron powder diffraction pattern of $\text{Sr}_3\text{NiIrO}_6$.¹⁹ Note,

that the isostructural $\text{Ca}_3\text{CoIrO}_6$ compound with a shorter Co-Co interchain distance in comparison to $\text{Sr}_3\text{CoIrO}_6$ shows a higher degree of frustration, leading to a dominant short-range magnetic order and the absence of significant contributions to magnetic Bragg reflections in neutron powder diffraction patterns at low temperatures.

Our low-temperature neutron powder diffraction data provided indications for the presence of an orbital magnetic moment of Co in $\text{Sr}_3\text{CoIrO}_6$. We also argue that parts of the sample might show order after a long relaxation time as magnetic reflections of such one-dimensional oxides exhibit clear time dependence.³⁹ For example, a time-dependent magnetic transition from one long-range ordered state to another in a zero magnetic field, occurring over a time interval of several hours, was observed for $\text{Ca}_3\text{Co}_2\text{O}_6$.³⁹

ACKNOWLEDGMENTS

A.T. was supported by the Alexander von Humboldt Foundation. The authors are indebted to N. Hollmann (Max Planck Institute for Chemical Physics of Solids, Dresden, Germany) for fruitful discussion.

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